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Progress Report

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Publications:

a) The Analysis of Complex Organic Compounds by Fast-electrical-scanning High resolution Mass Spectrometry and Gas Chromatography.

Lipsky, S.R., McMurray, W.J. and Horvath, C.G. Proceedings of the Sixth International Symposium on Gas Chromatography and Associated Techniques. P. 299-317, 1966. Editor: A.B. Littlewood, Elsevier Publishing Co., Amsterdam.

b) Fast Scan High Resolution Mass Spectrometry: II. Results Obtained with Direct Data Acquisition Systems.

McMurray, W.J., Lipsky, S.R. and Green, B.N. Advances in Mass Spectrometry, Volume 4, September 1967, Elsevier Publishing Co., Amsterdam, Holland (reprints will be available by December, 1967).

c) Fast Liquid Chromatography: I. An Investigation of Operating Parameters and the Separation of Nucleotides on Pellicular Ion Exchangers.

Horvath, C.G., Preiss, B. and Lipsky, S.R. Analytical Chemistry, Vol. 39, October 1967 (reprints will be available in November 1967).

Enrichment Devices:

Stop-Start Gas Chromatography and its use with Mass Spectrometry and Infra-red for the separation and identification of organic compounds - a possible alternative to the use of enrichment devices

As pointed out previously, a very essential part of the tandemly operated gas chromatograph-mass spectrometer instrument is the enrichment system used to interface the two instruments. Ideally, this system should be capable of selectively and dynamically removing much of the carrier gas (helium or hydrogen) from the gas chromatographic column effluent with little or no loss of the sample solute (sample enrichment) prior to entry into the ion source of the mass spectrometer. This is necessary for the maintenance of an adequate vacuum in the mass spectrometer in order to provide good interpretable fragmentation patterns at relatively high sensitivity.

In the area of flight instrumentation, one basic problem that confronts one here is the need for a reliable, sustainable pumping system to maintain the enrichment device (in addition to the ion source of the mass spectrometer) at optimum efficiency. Recently, Dr. R.P.W. Scott of England described a unique gas chromatographic system which can be coupled to a mass spectrometer without the use of enrichment devices and its associated pumping requirements. During the last several months we have explored this system and found that it has many features attractive to the GC-MS program. It was noted that by automatically interrupting the elution of the solute bands from the gas chromatographic column with no loss of resolving power, each peak was automatically trapped out in a special short length of packed column, concentrated by freeing it from the carrier gas, and then automatically eluted into the ion source of the mass spectrometer (and a special infrared cell as well). Under these circumstances each solute peak could be examined for a minimum of 10 minutes before the next peak was eluted. Such conditions were obtained by the use of a sequence programmer which automatically stopped the chromatographic development (by stopping the carrier gas flow) after each peak and starting it again after adequate spectra have been attained.

Upon theoretical grounds, it is obvious that certain aspects of this concept warrant close scrutiny as possible trade-offs for the Gas Chromatography-Mass Spectrometry program. At this time, its major advantages appear to be the following:

- 1) no requirement for enrichment devices and associated pumping
- 2) 95 to 100% transmission of the eluted solute peak into the mass spectrometer over a time interval that could extend from 10 seconds to 10 minutes
 - a) accordingly, sample overload and underload possibilities are minimized since with appropriate valving any portion of the band may be fed into the mass spectrometer on a 'time' basis.
- 3) complete on line telemetry control of the device from Earth because of the very favorable time factors involved
 - a) here, for example, a portion of the solute band is admitted into the mass spectrometer. The further elution from the chromatographic column is stopped and a mass spectral scan is obtained and the results are then telemetered back to Earth (approximately 4 minutes). The data is analyzed and appears to be satisfactory. A signal from Earth is then transmitted to the device to proceed with the analysis (4-6 minutes). Carrier gas flow thru the column is then restored and further elution of sample component bands continues on a stop start basis. Thus, under these circumstances, scientists could now have the capability of viewing the results of

any part of the 'run' prior to continuing with any further analysis. Accordingly, depending upon the nature of the results that are forthcoming, programmed sequences may be readily altered by Earth ground control to accommodate a wide variety of situations that may arise.

4) conservation of carrier gas and data handling resources may be readily attained

5) additional capabilities to handle many more sample cycles via the stop start procedure. Here, with appropriate instrument design and valving, one can accept or reject a sample analysis by appropriately directing the column effluent into or away from the mass spectrometer

6) possibly less stringent requirements for mass spectrometer design (particularly in the area of scan speed versus sensitivity)

7) additional sophistication may be obtained on more advanced missions by conveniently adding infra-red analysis. This could provide further information concerning the nature of the chemical structure of possible organic compounds found in the Martian soil.

The possible disadvantages of this particular system may be:

a) the necessity for additional valving and flow control devices

b) the possible complexity induced with the trapping procedure.

In essence then, it appears that such a system may possess many advantages for the overall GC-MS program. With the guidance of Dr. R.P.W. Scott, we will continue to investigate all of the operating parameters that are involved here and to assess the role of this system in facilitating the procurement of additional information concerning the structure of complex organic compounds of biochemical interest.

Pyrolysis Studies:

This program is continuing as outlined in the previous progress report. This involves an assessment of the design of a pyrolysis system for this experiment as well as certain operating parameters such as

- a) nature of carrier gas and flow rates
- b) sample size

- c) temperature
- d) duration of pyrolysis
- e) the effect of inorganic constituents on pyrolysis patterns

The Rapid Detection of Non-Volatile Compounds by Liquid Chromatography

In an effort to eventually achieve as complete an analysis of organic compounds present in surface material as possible an attempt was made to try to detect those non-volatile substances that are not readily amenable to analysis by gas chromatography and mass spectrometry. Accordingly, a liquid chromatographic system featuring high inlet pressures and a sensitive UV detector was designed for fast analysis of non-volatile organic compounds. To establish optimal operating conditions, band dispersion in the mobile phase was studied by using capillary tubes as well as small bore columns packed with glass beads. Although peak broadening in open tubes was less than predicted by theory, the use of packed columns was more promising for fast separations. Novel pellicular column materials were prepared by coating glass beads with ion exchange resin and other solid phases. Rapid separation of nanomole quantities of ribonucleoside mono-, di-, and triphosphates was achieved by using a pellicular basic ion exchanger and gradient elution with a phosphate buffer. As shown by cellular extract analyses, the stability and efficiency provided by such column materials makes it possible to achieve fast separation of complex mixtures by a liquid chromatographic technique similar in speed, resolution, and quantitative range to gas chromatography.